

PATENT SPECIFICATION

NO DRAWINGS

906.425



Date of Application and filing Complete Specification Dec. 11, 1958.

No. 40078/58.

Application made in Germany (No. W22396) on Dec. 11, 1957.

Complete Specification Published Sept. 19, 1962.

Index at acceptance:—Classes 1(1), A3B1; and 2(6), P7D(1A:1B:1X:2A1), P7K(4:8:10), P7P(1A:1B:1C:1F:1X:3:6A), P7T1C, P10(D1A:K7), P10P(1A:1B:1C:1F:1X:3:6A), P10T1C, P13D(2A:2B:2C:2X:3:4:5A), P13DX, P13G(4X:6), P13(H3:N4), P13R2(A:B), P13T1B.

International Classification:—B01j. C08f.

COMPLETE SPECIFICATION

Process for Polymerising Unsaturated Organic Compounds, and Catalysts Therefor

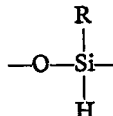
We, WACKER-CHEMIE G.M.B.H., a Company recognised by German law, of 22, Prinzregentenstrasse, Munich 22, Germany do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The polymerisation of α -olefines and other compounds of the vinylic type has been the subject of much research and extensive publication. It is known that certain olefines and other vinyl compounds can be polymerised in various ways to form products of higher molecular weight.

One commercial method for making such polymers involves heating the monomer at temperatures up to 200° C. and pressures up to 100 atmospheres in the presence of certain organic solvents, such as gasoline, Diesel oil or aromatic hydrocarbons, and using a catalyst prepared by mixing (component A) a metal or compound of an element of the Group IA, IIB, IIIA or IVB of the Periodic Table of the elements and (component B) a compound of a metal of sub-group IVA, VA or VIA of the Periodic Table. Well known and widely used as components A are organo-metal compounds, especially alkyl compounds of aluminium, magnesium, zinc, tin, lead, sodium, potassium or other alkali metal. Examples of the components B are compounds of titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten and uranium. It is known that mixtures of components A and B suffer from certain disadvantages, such as extreme toxicity, flammability, and difficulty in the preparation of the ultimate catalyst.

This invention provides a process for poly-

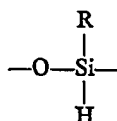
merising or copolymerising olefines and other vinyl monomers or mixtures thereof containing ethylene groups, with the aid of a catalyst, wherein there is used as catalyst a reaction product of (A) a hydrogen-containing siloxane polymer containing identical or different structural units of the general formula



in which R represents a hydrogen atom or an alkyl, cycloalkyl, aryl alkoxy, cycloalkoxy or aryloxy group which may be substituted, with (B) a compound of a metal of Group IVA, VA or VIA of the Periodic Table and wherein there is incorporated with the catalyst and/or added during the polymerisation a further quantity of a compound of a metal of Group IVA, VA or VIA of the Periodic Table in a lower valency stage and/or a Friedel-Crafts catalyst, the proportion of said addition being within the range of 0.001 to 100%, calculated on the weight of component B and/or the formation of the catalyst is carried out in the presence of up to 20% of a hydrogen donor, calculated on component B. The invention also includes the catalysts when used for carrying out the polymerisation process.

The catalysts of this invention are very active, and are used in the absence of moisture and air. The catalysts are especially useful for the manufacture of high polymers and copolymers of olefines, such as ethylene and other vinyl monomers.

The hydrogen-containing siloxane polymer contains units of the formula



in which each R represents a hydrogen atom or an alkyl group such as methyl, ethyl, propyl or octadecyl; a cycloalkyl group, such as cyclopentyl or cyclooctyl; an aryl group, such as phenyl or anthracyl group; an alkoxy group; a cycloalkoxy group; an aryloxy group; or a substituted product of such a group, such as the chlorophenyl or tolyl group.

The siloxane may be a homopolymer of repeating identical units, such as methyl-hydrogen-siloxane polymer, or a copolymer containing, for example 80 mol % of methyl-hydrogen-siloxane units, 15 mol % of phenyl-hydrogen-siloxane units, 3 mol % of methoxy-hydrogen-siloxane units, 1.5 mol % of cyclopentyl-hydrogen-siloxane units and 0.5 mol % of dimethyl-hydrogen-siloxane units. Examples of other units that may be present are 3:3-trifluoropropyl-hydrogen-siloxane units, methyl-phenyl-hydrogen-siloxane units, octadecyl-hydrogen-siloxane units, cyclooctyl-hydrogen-siloxane units, ethoxy-methyl-hydrogen-siloxane units, chlorophenyl-hydrogen-siloxane units, iodomethyl-hydrogen-siloxane units or dibromophenyl-hydrogen-siloxane units. Mixtures of homopolymers or of copolymers of homopolymers and copolymers may be used. Small amounts of up to 20 mol per cent of units containing no silicon-bonded hydrogen may be present.

The second component of the catalyst system is a compound of a metal in the Groups IVA, VA and VIA of the Periodic Table. Examples of such compounds are halides, such as titanium tetrachloride, zirconium tetrachloride, vanadium tetrachloride, chromium tetrachloride, molybdenum pentachloride and hafnium tetrachloride, and also the corresponding fluorides, bromides or iodides of these metals; oxyhalides, such as zirconium oxychloride, vanadium oxychloride and chromium oxychloride; alcoholates, such as the butylates, n-octylates, cyclohexylates, butenylates, 2-cyclohexenylates, hexylates and 2-phenylethylates of metals, such as Ti, Zr, V, Cr, Mo or U; acetylacetonates, such as zirconium, thorium or chromium acetylacetonate; and halogen-containing cyclopentadienyl metal compounds such as dichloro-bis-(cyclopentadienyl) compounds of titanium, zirconium or vanadium. Single compounds or mixtures of compounds can be used.

The catalysts are easily prepared. It is necessary that at least 0.5 mol of RHSiO units be present for each mol of the metal compound, and there is preferably an excess of RHSiO units. The hydrogen-siloxane polymer and the metal compound are dissolved or suspended in a substantially anhydrous inert

solvent, such as gasoline, and are deaerated and heated in the reaction vessel in which the polymerization is to be carried out. The mixture of components A and B in the solvent is heated at a temperature within the range of 60° C. to 150° C. and preferably 90° C. to 110° C. for 1 to 2 hours. The catalysts are obtained in heterogeneous phase or in solution and there is then incorporated 0.01—100 per cent, calculated on the weight of compound B, of a further quantity of a compound of a metal of Group IVA, VA or VIA of the Periodic Table in the lower valency stage and/or a Friedel-Crafts catalyst, such as TiCl_3 , TiCl_2 , VCl_3 , CrCl_3 , AlCl_3 or ZnCl_2 , to the mixture of components A and B before heating, and/or the formation of the catalyst is carried out by adding a small proportion of the hydrogen donor, that is to say, an organic compound containing "active hydrogen" is determined by the Zerewitinoff reaction, such as a substantially anhydrous aliphatic alcohol, for example, methyl alcohol, to the mixture before heating. The hydrogen donor may be present in proportions up to 20 per cent of the weight of component B.

The hydrogen-siloxane polymer is thereby further activated and used more efficiently, the yield of catalyst is increased and the polymerisation accelerated.

Furthermore, the addition of an equal weight of component B to the prepared catalyst mass followed immediately by initiation of the polymerisation, produces an improved space-time yield of product.

The preceding description relates to the preparation of the catalyst preceding the polymerisation reaction. Alternatively, the catalyst components and the monomer or monomeric mixture to be polymerised may be placed in the reaction zone and the formation of the catalyst and the polymerisation of monomer or monomers be brought about concurrently. This procedure is especially suitable for carrying out the polymerisation in a continuous manner by continuously supplying fresh catalyst components and monomer or monomers to the reaction zone and continuously removing the polymer and exhausted catalyst therefrom.

This polymerisation process is applicable generally to olefines and other vinyl monomers. Thus, by this process olefines, such as ethylene, propylene, butene-(1), hexene-(1), heptene-(1), octene-(1) or isobutylene, and also as aliphatic olefine derivatives, such as vinyl chloride, vinyl acetate, and acrylic derivatives such as acrylonitrile, can be polymerised or copolymerised. The process can also be applied to vinyl aromatic compounds, such as styrene and derivatives thereof.

The polymerisation reaction is carried out by maintaining the monomer or monomers in contact with the catalyst system. A pressure of 1 to 100 atmospheres and a tempera-

ture of 30° C. to 200° C. may be used. Good results have been obtained with pressures of 10 to 50 atmospheres and temperatures of 65° to 130° C.

5 The polymerisation products so obtained can be separated from the reaction mixture and purified by methods well known in the art. When the polymerisation reaction is carried out under a pressure of 10 atmospheres or higher, the polymerisation product can be subjected to mechanical comminution in an alcoholic suspension, after separation from the solvent. However, if the reaction pressure is lower than 10 atmospheres, the polymer will be pulverulent and especially easy to separate from the catalyst residues.

The polymerisation products exhibit a peculiar linear structure which is evident from their high softening and melting points. The ash content of the purified polymers is exceedingly low, being less than 0.1% and %90'0 pur 40'0 usatied. Sined ly llareag

The following examples illustrate the invention, the parts and percentages being by weight. All viscosities are measured at 25° C.

EXAMPLE 1.

A stainless steel autoclave of one litre capacity provided with a magnetic stirring apparatus was used and 12.5 cc of dried and deaerated methyl-hydrogen-polysiloxane (viscosity of 30 centipoises), 1.25 g of TiCl_4 , and 340 cc of dried, deaerated gasoline (boiling range 150° to 180° C.) were placed therein under dry nitrogen. 10 cc of a suspension of 10% strength of a mixture of TiCl_3 and TiCl_2 (ratio of 5.4:1) in gasoline were then added to the catalyst mixture. The mixture was heated in the closed autoclave for 1.5 hours at 105° C. under autogenous pressure. Ethylene was then forced into the autoclave under a pressure of 24 atmospheres. The polymerisation was carried out over a period of 24 hours at a temperature of 123° C. to 134° C. and a pressure of 39 atmospheres, and additional quantities of ethylene were forced into the reaction zone from time to time. The reaction mass was cooled to 20° C. and the excess ethylene was released. The product was a solid grey polyethylene. The polymer was separated from the solvent by filtration, and was further purified by washing it with methanol, boiling it under reflux for 1 hour with a mixture of equal parts of nitric acid of 10% strength and methanol, and then neutralising with methanol and water. The product was dried at 85° C. and 32 grams of a white polymer of high molecular weight were obtained having a fusion point of 136° C. and an ash content of less than 0.1%. No constituents of low molecular weight could be detected even by the use of boiling acetone. The fusion point was determined by the extinction of double

refraction observed under a polarising microscope.

When the above procedure was repeated without the methyl-hydrogen-siloxane, the polymer was obtained but in a yield amounting to only about 3% of the yield obtained when the methyl-hydrogen-siloxane formed part of the catalyst system.

EXAMPLE 2.

The process of Example 1 was repeated with 1 gram of sublimed, finely divided AlCl_3 , instead of the mixture of low valency titanium chlorides. The ethylene was supplied for 2 hours at 105° C. and at a pressure of up to 47 atmospheres. The reaction was carried out at 125° C. and 50 atmospheres for 18 hours. The raw product was a reddish brown material which was separated and purified as before. The solid polyethylene obtained in a yield of 34 grams had a fusion point of 130° C.

When the above procedure was repeated without the methyl-hydrogen-polysiloxane, no solid product was obtained.

EXAMPLE 3.

The catalyst was prepared as described in Example 1, and a solution of 1.25 grams of TiCl_4 dissolved in 15 cc of gasoline was added to the catalyst at 100° C. Ethylene was introduced into the autoclave to a pressure of 24 atmospheres. The polymerisation was carried out for 16 hours under the conditions of temperature and pressure, given in Example 1. The purified product obtained in a yield of 34 grams was a polyethylene of high molecular weight having a fusion point of 134° C.

EXAMPLE 4.

An autoclave as described in Example 1 was scavenged with nitrogen and charged with 5 cc of the methyl-hydrogen-polysiloxane identified in Example 1, 1.7 grams of TiCl_4 , 0.5 cc of anhydrous methanol and 350 cc of gasoline under nitrogen. The mixture was heated for 1 hour at 100° C. under autogenous pressure in the closed and locked autoclave. A further 1.7 grams of TiCl_4 were then added at 100° C. and ethylene was forced into the autoclave up to 10 atmospheres pressure. The reaction mixture was heated at 100° C. for 21 hours under 10 atmospheres pressure with the periodic addition of further ethylene to maintain the said pressure. The mixture was cooled and the excess of ethylene was vented off. The resulting polymer was a solid, brown polyethylene. The polymer was separated from the solvent and triturated in the presence of methanol. By purifying the product as described in Example 1, 71.5 grams of a white polyethylene of high molecular weight having a fusion point of 130° C. were obtained.

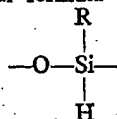
EXAMPLE 5.

An autoclave was charged with 12.5 cc of methyl-hydrogen-polysiloxane (30 centipoises) 1.7 grams TiCl_3 , 10 cc of a suspension of 10% strength of TiCl_3 and TiCl_4 in gasoline (the $\text{TiCl}_3 : \text{TiCl}_4$ ratio being 5.4:1), and 340 cc of gasoline (boiling range 150° to 180° C.), under dry nitrogen. The mixture was heated to 110° C. for 2 hours in the locked autoclave. The mixture was cooled to 50° C. A mixture of ethylene and vinyl chloride was forced into the autoclave to a pressure of 15 atmospheres. The mixture was then heated at 75° C. under 20 atmospheres for 33 hours, further ethylene being added to maintain the reaction pressure. The mixture was cooled and the excess of monomeric material was vented off. 30 grams of a brownish, solvent-saturated polymeric material was obtained and was separated and purified as in Example 1. A good yield of a yellow copolymer was obtained. The chlorine content of the copolymer indicated that it contained 89 per cent polymerised vinyl chloride and 11 mol per cent of polymerised ethylene.

Specification No. 830,424 describes and claims a process for polymerising a polymerisable compound characterised in that the polymerisable compound is brought into contact with a catalyst produced by a process characterised in that at least one silicon compound containing the group $\text{H}-\text{Si}-$ where the residual valencies are satisfied by $-\text{R}$, $-\text{Si}-$, $-\text{OR}$ or $-\text{O}-\text{Si}-$ groups, where R is an alkyl, cycloalkyl, aryl or acalkyl group, and where the residual valencies on the said groups are similarly satisfied, is treated with a compound of a transition metal occupying any of the 4th and 6th places after the inert gases in one of the long periods of the periodic system of the elements, it being understood that the rare earth metals occupy one place therein.

WHAT WE CLAIM IS:—

1. A process for polymerising or copolymerising olefines and other vinyl monomers with the aid of a catalyst, wherein there is used as catalyst a reaction product of (A) a hydrogen-containing siloxane polymer containing identical or different structural units of the general formula



in which R represents a hydrogen atom or an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy or aryloxy group which may be substituted with, (B) a compound of a metal of Group IVA, VA or VIA of the Periodic Table and wherein there is incorporated with the catalyst and/or added during the polymerisation a

further quantity of a compound of a metal of Group IVA, VA or VIA of the Periodic Table in a lower valency stage and/or a Friedel-Crafts catalyst, the proportion of said addition being within the range of 0.001 to 100%, calculated on the weight of component B and/or the formation of the catalyst is carried out in the presence of up to 20% of a hydrogen donor, calculated on component B.

2. A process as claimed in Claim 1, wherein component A of the catalyst consists of units of the said formula and not more than 20 mol per cent of units containing no hydrogen bound to silicon.

3. A process as claimed in Claim 1, wherein the catalyst is a reaction product of at least 0.5 molecular proportion of component A with one molecular proportion of component B.

4. A process as claimed in Claim 3, wherein the catalyst contains more than 0.5 molecular proportion of component A per molecular proportion of the component B.

5. A process as claimed in any one of Claims 1—4, wherein component B of the catalyst is a halide of titanium, zirconium, vanadium, chromium, molybdenum, hafnium or uranium.

6. A process as claimed in any one of Claims 1—4 wherein component B of the catalyst is an oxyhalide, alcoholate, acetylacetate or halogen-containing cyclopentadienyl metal compound of titanium, zirconium, vanadium, chromium, molybdenum, hafnium or uranium.

7. A process as claimed in any one of Claims 1—6, wherein the reaction product which constitutes the catalyst is formed before the polymerisation.

8. A process as claimed in any one of Claims 1—6, wherein the polymerisation process is continuous, and the formation of the reaction product which constitutes the catalyst and the polymerisation of the monomer or monomers takes place simultaneously.

9. A process as claimed in any one of Claims 1—8, wherein an aliphatic alcohol, for example, methyl alcohol, is used as hydrogen donor.

10. A process as claimed in any one of Claims 1—9, wherein there is added to the catalyst before the addition of the monomer or monomers or during the polymerisation a further catalytic quantity of a compound of a metal of group IVA, VA or VIA of the Periodic Table in its highest valency stage.

11. A process as claimed in any one of Claims 1—10, wherein titanium trichloride, titanium dichloride, vanadium trichloride, chromium dichloride, aluminium chloride or zinc chloride is used as the said addition.

12. A process as claimed in any one of Claims 1—11, wherein the polymerisation is

carried out in the presence of an auxiliary liquid.

13. A process as claimed in any one of Claims 1—12, wherein the polymerisation is
5 carried out at a temperature within the range of 30° C. to 200° C. under a pressure within the range of 1 to 100 atmospheres gauge pressure.

14. A polymerisation process according to
10 Claim 1 conducted substantially as des-

cribed in any one of the examples herein.

15. A polymerisation catalyst, which comprises a reaction product of a component A and a component B as herein defined and used
11. as claimed in any one of Claims 1—9 and 15

ABEL & IMRAY,
Chartered Patent Agents,
Quality House, Quality Court, Chancery Lane,
London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1962.

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained